$C_{32}H_{36}O_4P_2PdS_4$

Les longueurs des deux liaisons P—S sont comparables ce qui signifie que les atomes de soufre* sont dicoordinés et non pas di- et tricoordinés comme cela est observé dans d'autres complexes métalliques stabilisés par un ligand analogue (Lefferts, Hossain, Molloy, van der Helm & Zuckerman, 1980). Dans ces conditions, les conclusions que l'on peut tirer de cette structure en ce qui concerne l'atome de phosphore sont transposables au modèle (I).

Pour ce qui est de l'environnement de l'atome de phosphore, les deux cycles phényle sont situés dans deux plans sensiblement perpendiculaires (95°) de sorte que les substituants en position 2 et 6 sur chaque cycle réalisent une 'protection' autour de l'atome de phosphore. Cet arrangement est bien la conséquence d'interactions stériques entre cycles phényle et non pas le fait d'interactions stabilisantes de type π entre cycles

phényle appartenant à des molécules voisines dans le cristal.

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μ-Oxo-μ-sulphido-bis{[(O,O'-diisopropylphosphorodithioato)-S,S']oxomolybdenum(V)}

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Abstract. [{Mo(O)[S$_2$P(OC$_3$H$_7$)$_2$]}$_2$OS], $M_r = 698\cdot3$, orthorhombic, Pbca, $a = 23\cdot021$ (11), $b = 16\cdot030$ (9), $c = 14\cdot792$ (12) Å, $U = 5458\cdot6$ Å^3, $Z = 8$, $d_m = 1\cdot68$ (3), $d_c = 1\cdot70$ Mg m^{-3}, Mo Kα radiation, $\lambda = 0\cdot7107$ Å, $\mu = 1\cdot29$ mm^{-1}, $F(000) = 2800$; systematic absences: $h0l, l = 2n + 1, hk0, h = 2n + 1, 0kl, k = 2n + 1$. $R = 0\cdot083$ for 1001 reflections. In the binuclear complex the two Mo atoms are bridged via one S atom [2·370 (4), 2·333 (4) Å] and one O atom [1·967 (10), 2·011 (10) Å]. There is also a weak interaction between the Mo atoms [Mo···Mo 2·690 (2) Å]. The coordination sphere around each Mo atom is completed by a terminal O atom [1·654 (8), 1·632 (8) Å] and two S atoms from the bidentate ligand. The geometry around the metal atoms is distorted square pyramidal.
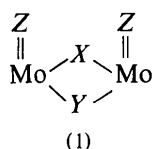
Introduction. The complex [{Mo(O)[S$_2$P-(OC$_3$H$_7$)$_2$]}$_2$OS] was prepared during an investigation of molybdenum–sulphur compounds of possible value as soluble friction- and wear-reducing additives to lubricating oils (Black, Dunster & Sanders, 1969). Crystals were obtained from the reaction of aqueous

solutions of sodium molybdate and diisopropyl-phosphorodithioic acid. Details of the preparative chemistry and properties of this and related compounds will be reported elsewhere.

A crystal approximately 0·1 × 0·5 × 0·2 mm was mounted with the (100) planes parallel to the instrument axis of a General Electric XRD5 diffractometer. 1907 independent reflections with $2\theta < 35°$ were measured by the stationary-crystal–stationary-counter method with 10 s counts. Of these, 1001 with $I > 2\sigma(I)$ were used in subsequent calculations. The positions of the metal atoms were located from the Patterson map and those of all other atoms except H were obtained from subsequent Fourier maps. H atoms were included in the calculation in tetrahedral positions with thermal parameters fixed at values equivalent to those of the C atoms to which they were bonded. For five of the eight methyl groups the H atoms were successfully refined as rigid groups. H atoms from the remaining three groups were not located. The final R with Mo, S, P anisotropic and C, O isotropic was 0·083. The weighting scheme was $w^{1/2} = 1$ for $F_o < 80$ and $w^{1/2} = 80/F_o$ for $F_o > 80$.

This gave satisfactory constant values of $w\Delta^2$ over groups of $\sin\theta/\lambda$ and F_o. Calculations were carried out on a CDC 7600 computer at the University of London Computer Centre using *SHELX* 76 (Sheldrick, 1976). Atomic scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The final atomic positions are given in Table 1, bond lengths and angles in Table 2.* A view of the molecule is given in Fig. 1.

Discussion. The title compound (I) belongs to a well established group of compounds containing the moiety (1) (Spivak & Dori, 1975). Examples are known with Z

$$
\begin{matrix}
Z & & Z \\
\| & X & \| \\
Mo & & Mo \\
& Y &
\end{matrix}
$$

(1)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36064 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates (for* Mo $\times 10^5$, *for other atoms* $\times 10^4$) *and isotropic thermal parameters* $(\mathring{A}^2 \times 10^3)$

For Mo, S and P atoms $\bar{U} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	$\bar{U}(\times 10^3)$
Mo(1)	12153 (5)	58618 (7)	74198 (8)	41 (2)
Mo(2)	14844 (5)	43812 (7)	81669 (8)	37 (2)
S(21)	825 (1)	3168 (2)	8270 (2)	47 (5)
S(22)	2166 (2)	3217 (2)	7790 (2)	43 (5)
P(2)	1517 (1)	2434 (2)	8084 (2)	31 (4)
S(11)	233 (1)	6332 (2)	6898 (3)	62 (5)
S(12)	1454 (1)	6497 (2)	5940 (3)	62 (5)
P(1)	653 (2)	7002 (2)	5945 (2)	48 (5)
S(1)	2060 (2)	5069 (3)	7105 (3)	70 (5)
O(3)	728 (4)	4961 (6)	7911 (6)	77 (3)
O(1)	1352 (3)	6529 (5)	8246 (6)	60 (3)
O(2)	1658 (4)	4617 (5)	9206 (5)	55 (3)
O(21)	1450 (3)	1722 (4)	7351 (4)	24 (2)
O(12)	642 (4)	7957 (6)	6232 (5)	52 (3)
O(11)	357 (3)	6978 (6)	5001 (6)	53 (3)
O(22)	1594 (3)	1878 (5)	8960 (5)	44 (2)
C(21)	1352 (4)	1972 (6)	6417 (7)	15 (3)
C(14)	988 (5)	8553 (8)	5720 (9)	46 (4)
C(15)	1434 (6)	8988 (10)	6292 (10)	85 (5)
C(22)	837 (5)	1601 (9)	6049 (8)	46 (4)
C(24)	2091 (5)	1215 (8)	9029 (9)	45 (4)
C(23)	1903 (6)	1630 (9)	6011 (9)	53 (4)
C(16)	530 (7)	9164 (11)	5284 (11)	93 (6)
C(25)	1742 (6)	380 (10)	8989 (11)	86 (5)
C(12)	542 (9)	6383 (12)	3532 (13)	129 (7)
C(13)	−352 (9)	6050 (14)	4427 (15)	152 (9)
C(26)	2429 (9)	1418 (15)	9921 (14)	148 (8)
C(11)	317 (6)	6294 (10)	4434 (10)	68 (5)

Table 2. *Interatomic distances (Å) and angles (°)*

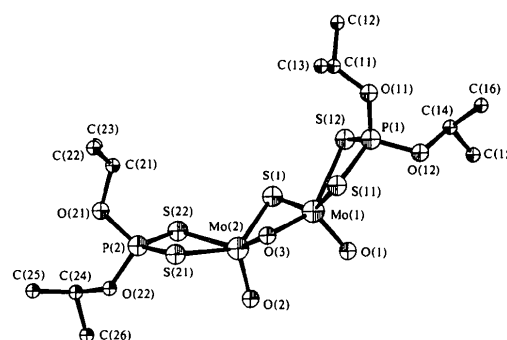|			
Mo(1)–Mo(2)	2·690 (2)		
Mo(1)–S(11)	2·505 (3)	Mo(1)–O(3)	1·967 (10)
Mo(1)–S(12)	2·476 (4)	Mo(1)–O(1)	1·654 (8)
Mo(1)–S(1)	2·370 (4)		
S(11)–Mo(1)–S(12)	78·72 (12)	S(1)–Mo(1)–O(3)	98·5 (3)
S(11)–Mo(1)–S(1)	147·32 (14)	S(11)–Mo(1)–O(1)	101·8 (3)
S(12)–Mo(1)–S(1)	82·20 (13)	S(12)–Mo(1)–O(1)	110·2 (3)
S(11)–Mo(1)–O(3)	79·6 (3)	S(1)–Mo(1)–O(1)	109·6 (3)
S(12)–Mo(1)–O(3)	139·0 (3)	O(3)–Mo(1)–O(1)	108·1 (4)
Mo(2)–S(21)	2·472 (3)	Mo(2)–O(3)	2·011 (10)
Mo(2)–S(22)	2·501 (4)	Mo(2)–O(2)	1·632 (8)
Mo(2)–S(1)	2·333 (4)		
S(21)–Mo(2)–S(22)	79·17 (11)	S(21)–Mo(2)–O(2)	105·9 (3)
S(21)–Mo(2)–S(1)	139·71 (14)	S(22)–Mo(2)–O(2)	103·3 (3)
S(22)–Mo(2)–S(1)	81·17 (13)	S(1)–Mo(2)–O(2)	112·7 (3)
S(21)–Mo(2)–O(3)	81·0 (3)	O(3)–Mo(2)–O(2)	106·4 (4)
S(22)–Mo(2)–O(3)	147·8 (3)	Mo(1)–S(1)–Mo(2)	69·79 (12)
S(1)–Mo(2)–O(3)	98·4 (3)	Mo(1)–O(3)–Mo(2)	85·1 (4)
S(21)–P(2)	1·999 (5)	O(11)–C(11)	1·38₀ '5)
S(22)–P(2)	1·999 (5)	O(22)–C(24)	1·565 (13)
P(2)–O(21)	1·583 (7)	C(21)–C(22)	1·434 (14)
P(2)–O(22)	1·582 (8)	C(21)–C(23)	1·506 (15)
S(11)–P(1)	2·018 (5)	C(14)–C(15)	1·501 (16)
S(12)–P(1)	2·015 (5)	C(14)–C(16)	1·578 (17)
P(1)–O(12)	1·590 (9)	C(24)–C(25)	1·563 (18)
P(1)–O(11)	1·554 (9)	C(24)–C(26)	1·564 (20)
O(21)–C(21)	1·456 (11)	C(12)–C(11)	1·439 (20)
O(12)–C(14)	1·457 (13)	C(13)–C(11)	1·588 (23)
Mo(2)–S(21)–P(2)	87·97 (15)	P(2)–O(21)–C(21)	117·8 (6)
Mo(2)–S(22)–P(2)	87·19 (16)	P(1)–O(12)–C(14)	118·9 (7)
S(21)–P(2)–S(22)	104·86 (20)	P(1)–O(11)–C(11)	126·4 (9)
S(21)–P(2)–O(21)	116·2 (3)	P(2)–O(22)–C(24)	121·2 (6)
S(22)–P(2)–O(21)	112·1 (3)	O(21)–C(21)–C(22)	111·9 (8)
S(21)–P(2)–O(22)	108·0 (4)	O(21)–C(21)–C(23)	98·5 (8)
S(22)–P(2)–O(22)	116·6 (4)	C(22)–C(21)–C(23)	113·2 (9)
O(21)–P(2)–O(22)	99·5 (4)	O(12)–C(14)–C(15)	112·7 (10)
Mo(1)–S(11)–P(1)	86·77 (16)	O(12)–C(14)–C(16)	104·7 (9)
Mo(1)–S(12)–P(1)	87·62 (16)	C(15)–C(14)–C(16)	113·5 (11)
S(11)–P(1)–S(12)	103·11 (21)	O(22)–C(24)–C(25)	101·7 (9)
S(11)–P(1)–O(12)	108·5 (4)	O(22)–C(24)–C(26)	106·1 (11)
S(12)–P(1)–O(12)	113·7 (4)	C(25)–C(24)–C(26)	117·7 (12)
S(11)–P(1)–O(11)	114·0 (4)	O(11)–C(11)–C(12)	117·3 (13)
S(12)–P(1)–O(11)	112·8 (4)	O(11)–C(11)–C(13)	105·4 (13)
O(12)–P(1)–O(11)	104·9 (5)	C(12)–C(11)–C(13)	111·6 (15)

Fig. 1. A view of the molecule showing the atom-numbering scheme.

= O or S: $X = Y = $ O; $X = Y = $ S and $X = $ O, $Y = $ S. (I) contains the rare μ-oxo-μ-sulphido bridge. The dimensions of the Mo$_2$SO bridge in (I) are similar to those in [Mo(OS)O$_2$(dmdtc)$_2$] (dmdtc = N,N-dimethyldithiocarbamate) (Dirand-Colin, Ricard & Weiss, 1976). The bridge is folded so that the dihedral

Table 3. *Least-squares-planes calculations*

Distances of atoms from the planes are given in Å. Atoms not contributing to the plane are marked with an asterisk.

Plane 1: S(1) 0·04 (1); O(3) −0·04 (1); S(11) 0·04 (1); S(12) −0·04 (1); Mo(1)* 0·69 (1)
Plane 2: S(1) −0·10 (1); O(3) 0·11 (1); S(21) −0·11 (1); S(22) 0·10 (1); Mo(2)* 0·69 (1)
Plane 3: Mo(1), S(11), S(12), 0·00; P(1)* 0·46 (1)
Plane 4: Mo(2), S(21), S(22), 0·00; P(2)* 0·21 (1)
Plane 5: Mo(1), S(1), O(3)
Plane 6: Mo(2), S(1), O(3)
Plane 7: S(11), S(12), P(1)
Plane 8: S(21), S(22), P(2)

Angles between planes (°) (mean e.s.d. 0·1°): 3/4 67·9; 3/5 51·0; 3/6 17·8; 3/7 21·4; 3/8 58·0; 4/5 18·5; 4/6 50·2; 4/7 47·4; 4/8 9·9; 5/6 33·2; 5/7 29·8; 5/8 10·4; 6/7 4·6; 6/8 40·4; 7/8 37·8

angle between the two MoOS moieties is 148·0°, compared to 146·8° in (I).

The structure of (I) may also be compared with the di-μ-sulphido analogue (II) (Atovmyan, Tkachev & Shchepinov, 1978). The Mo—S$_{br}$ distance in (I) is slightly longer (2·351 vs 2·305 Å) and the metal–metal distance is shorter (2·690 vs 2·819 Å). Consequently, the Mo—S$_{br}$—Mo angle is more acute in (I) than in (II) [69·8 (1) vs 75·5°]. The Mo—O$_{br}$ distance is 1·989 (10) Å and the Mo—O$_{br}$—Mo angle is 85·1 (4)°. The different dimensions involving Mo—O and Mo—S are probably due to the size difference between O and S rather than any change in the nature of the bonding. It is surprising therefore that the fold angles in the bridge are similar [146·8 (I), 144·8° (II)].

The remaining dimensions in the dimer are as expected and are equivalent to those in (II). The metal atoms are bonded to a terminal O [1·654 (8), 1·632 (8) Å] and to two S atoms from the bidentate

ligand [2·472 (3) to 2·505 (3) Å]. If we ignore Mo··· Mo bonding, each Mo atom is five-coordinate square pyramidal with the terminal O atoms in axial positions. The Mo atoms are displaced 0·69, 0·69 Å out of the plane of the four equatorial atoms (3S, O) towards the terminal O atoms.

The MoS₂P four-membered rings are also puckered with the dihedral angles between the MoS₂ and S₂P planes 21·4 and 9·9°. Similar angles were found in (II), namely 21·9 and 9·0°, and we conclude, therefore, that the difference is due to packing effects. The other dimensions in the molecule are as expected. Details of least-squares planes are given in Table 3.

There are no intermolecular distances in the unit cell less than the sum of the van der Waals radii.

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Trimethyl-5,6,11 Pyrido[4,3-b]carbazole (Méthyl-6 Ellipticine)

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Abstract. $C_{18}H_{16}N_2$, monoclinic, $P2_1/c$, $Z = 4$, $a = 10·054$ (6), $b = 17·747$ (8), $c = 7·516$ (5) Å, $\beta = 93·40$ (7)°; $R = 0·07$ for 2099 independent reflections. The ellipticine skeleton is almost planar and stacks along the c axis.

Introduction. La méthyl-6 ellipticine (Fig. 1) possède une activité antitumorale sur la leucémie expérimentale L 1210 (Le Pecq, Dat Xuong, Gosse & Paoletti, 1974).

Ce composé se fixe sur l'ADN par intercalation entre les paires de base et son étude cristallographique entre dans le cadre plus général d'une étude de diverses ellipticines qui pourrait préciser le modèle d'intercalation de cette série de molécules.

Ce composé a été synthétisé par l'équipe du Dr N. Dat Xuong à l'Institut de Chimie des substances naturelles du CNRS de Gif-sur-Yvette. Les cristaux utilisables pour l'analyse radiocristallographique, ont